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Inventor: BARBARA SUSAN NEUMANN

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COMPLETE SPECIFICATION

Improvements in or relating to Synthetic Clay-like Minerals

We, THE FULLER'S EARTH UNION LIMITED, a British Company of Patteson Court, Nutfield Road, Redhill, Surrey, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to certain novel synthetic clay-like minerals and to processes for their synthesis.

It is an object of the invention to provide synthetic clay-like minerals which have very advantageous rheological properties in aqueous dispersion, particularly Bingham Yield Value.

We use the term synthetic clay-like mineral to denote materials having a structure similar to that of natural clay minerals. Thus the synthetic clay-like minerals can be ascribed a general formula in the same way as can natural clay minerals and their X-ray diffraction patterns will resemble those that would be expected of natural clay minerals of a similar general formula. For a discussion of natural clay minerals vide "The X-ray identification and crystal structure of clay minerals"; Mineralogical Society (G. Brown), 1961.

Novel synthetic clay-like minerals according to the invention have the general formula

$$\{Si_8[Mg_{6-x}.Li_x] . O_{20} . [(OH)_{4-y}F_y]\}^{x(-)} \frac{x}{n} . M^n(+)$$

in which M is a cation, x is a value greater than zero and less than 6, y is from 1.0 up to but less than 4 and n is an integer from 1 to 3. Preferably the cation M is sodium, n thus being equal to 1.

One synthetic clay-like mineral in accordance with the invention is

$$\{Si_8[Mg_{5.47}.Li_{0.53}] . O_{20} . [(OH)_2F_2]\}^{0.53(-)} . 0.53Na^{(+)}.$$

This synthetic clay, like others within the general formula above, has a structure that is shown by X-ray diffraction analysis and cation exchange capacity measurement to resemble that of naturally occuring hectorite.

However these synthetic products are not true hectorites, their fluoride-content is much higher than that of any naturally occurring hectorite. It is this characteristic which gives to synthetic products of the present invention, particularly when prepared by the process described below, greatly improved rheological properties over naturally occurring hectorites. The specific examples herein illustrate this.

The invention further provides a process for the synthesis of a clay-like mineral having a structure within the above general formula [F] when M = Na (and thus n = 1), which process comprises the steps of forming a slurry which contains constituents providing atomic ratios in the ranges

$$\frac{Si}{F} = 0.5 \text{ to } 5.1;$$

$$\frac{Li}{Mg} = 0.1 \text{ to } 1.0;$$

$$\frac{Si}{Mg+Li} = 0.5 \text{ to } 1.5;$$

$$\frac{Na}{2Mg+F-Li} = 1 \text{ to } 2$$

by co-precipitation by slowly combining with heating and agitation in an aqueous medium and in the presence of the lithium and fluoride ions, the constituent providing the magnesium ions with the constituents providing the silicon (as silicate), hydroxyl and sodium ions, hydrothermally treating the slurry for the period as herein defined, washing and dewatering the resultant product and then drying it at a temperature of substantially 110°C to 450°C. A preferred temperature range for this final step is 110°C to 250°C, and its purpose is to develop the rheological properties the clay will possess in aqueous dispersion.

Preferably the slurry will provide an atomic ratio of

$$\frac{Si}{F} \text{ of } 0.5 \text{ to } 4.0$$

and of

$$\frac{Na}{2Mg+F-Li} \text{ of } 1 \text{ to } 1.3.$$

By saying that the hydrothermal treatment is conducted for the period as herein defined is meant that it is conducted for at least that interval of time after which a sample of the product then existing (after filtering it, washing it and drying it at 110°C to constant weight) will form a gel upon being redispersed in water at 5% by wt. solids content. Normally the treatment will be conducted for at least 10 to 20 hours, preferably about 20 hours. Conveniently the hydrothermal treatment comprises boiling, with agitation, under reflux at atmospheric pressure. As the inevitable result of this hydrothermal treatment of the aqueous slurry, the final product will contain some hydroxyl ion and thus in the general formula quoted herein the value "y" will always be less than 4.

The slurry subjected to hydrothermal treatment is preferably formed by heating with agitation an aqueous medium containing the lithium, magnesium and fluoride ions, and slowly adding an aqueous solution of sodium silicate to this medium. Additional sodium ions, often as sodium carbonate, may also have to be added in order that the reaction mixture shall be sufficiently alkaline throughout. Advantageously the addition of sodium silicate is conducted over a period of at least 30 minutes, preferably about 1 hour. By increasing this period of time to 4 to 6 hrs. it is found that products having the higher Bingham Yield Value (in 2% gel form) can be obtained.

Conveniently the following compounds can be employed in the processes according to the invention:— Any suitable water-soluble magnesium salt, for example $MgCl_2.6H_2O$, $Mg(NO_3)_26H_2O$ or $MgSO_4.7H_2O$ for Mg^{++}; Li_2CO_3 or LiF for Li^+; HF acid or LiF, H_2SiF_6 or, for example, the sodium salt thereof, for F^-; Na_2CO_3, NaOH or sodium silicate for Na^+, and the latter also for silicon ions.

Desirably the dilution of the various constituents employed in forming the slurry is such that after the hydrothermal treatment the product is present in quantity of 1—8%, preferably 4% by weight.

When the cation of the resultant synthetic product is sodium the material is a hydrophilic swelling clay. Other cations can replace sodium, this being preferably effected by ion exchange after synthesis.

As illustrated by Examples I to V herein, swelling clays in accordance with the invention have Bingham Yield Values (measured as detailed in Example I) of from 50 to 150 dynes/sq.cm.

It is sometimes the case that the swelling properties of synthetic products in accordance with this invention can be greatly increased when used in solutions of high electrolyte content if the clay is pre-swollen before incorporation into the solution. Thus, for example, a pre-swollen gel having up to 25% by weight clay in water is a very convenient form of the product in practice.

The following examples illustrate processes in accordance with the invention:—

EXAMPLE 1.

14.5 g lithium fluoride was placed in a flask of about 5 litre capacity fitted with a stirrer, a heating mantle and a refluxing condenser. In a separate vessel 228 g magnesium chloride hexahydrate was dissolved in 1.5 litres of water and the solution added to the lithium fluoride. The mixture was brought to the boil under reflux; while stirring efficiently.

In a separate vessel 309 g sodium silicate solution containing 29 g SiO_2 and 8.8 g Na_2O per 100 g was diluted with 1.5 litres of water. This was added slowly to the reaction vessel containing the LiF and $MgCl_2$ solution. The addition was made over a period of about one hour, while the reaction mixture was kept boiling and stirred efficiently throughout.

A solution of 72 g anhydrous sodium carbonate in 1.1 litres of water was then made up and this was also added slowly, over a period of about one hour, to the reaction mixture.

The mixture was then boiled under reflux, with efficient stirring for 20 hours. After that, it was filtered under vacuum and washed by filtering 9 litres of water through the filter cake. Finally the filter cake was dried in trays at 130°C and ground in a small mill.

The finished product was tested by X-ray analysis and was found to have the same X-ray pattern as hectorite. It had a cation

exchange capacity of 70 m.e./100 g.

When 2 g was dispersed in 100 ml hot water, it was found that, after cooling, a clear thixotropic gel was obtained. The gel was heat stable and unaffected by electrolytes even when added in appreciable quantity. By using a rotational (Fann) viscometer, the following rheological parameters were measured on this dispersion:—

Plastic viscosity	13.5 centipoises
Bingham Yield Value	103.2 dynes/cm²

In this example the atomic ratios of the constituents in the feed are as follows:—

$$\frac{Si}{F} = 2.7;$$

$$\frac{Li}{Mg} = 0.5;$$

$$\frac{Si}{Mg+Li} = 0.9;$$

$$\frac{Na}{2Mg+F-Li} = 1.0.$$

The product obtained is

$$Si_8[Mg_{5.47}Li_{0.53}] \cdot O_{20} \cdot [(OH)_2F_2]^{0.53(-)}.0.53Na^{(+)}.$$

The improved rheological properties of this synthetic product can be judged from the fact that, even as a 3% by weight dispersion, a commercially available natural hectorite product had a plastic viscosity of only 5.0 centipoises and a Bingham yield value of only 33.6 dynes/cm².

EXAMPLE II.

In this example the procedure adopted was as for Example 1. However the quantity of lithium fluoride employed was in this case 11.6 g.

The atomic ratios of the constituents in the feed were thus:—

$$\frac{Si}{F} = 3.3;$$

$$\frac{Li}{Mg} = 0.4;$$

$$\frac{Si}{Mg+Li} = 0.95;$$

$$\frac{Na}{2Mg+F-Li} = 1.0$$

The product obtained had a cation exchange capacity of 52 m.e./100g; a 2% dispersion in water had a plastic viscosity of 10.0 centipoises and a Bingham yield value of 79.2 dyne/cm².

EXAMPLE III.

296 g. magnesium sulphate heptahydrate was dissolved in 1 litre water and placed in a flask of about 5 litres capacity fitted with a stirrer, a heating mantle and a refluxing condenser. In a separate vessel 26.5g lithium carbonate and 43.2g sodium hydroxide were added to 200 ml water and hydrofluoric acid solution was added to it under continuous stirring, until a neutral reaction was indicated by methyl red indicator. The amount required was approximately 240 ml of a 15% w/w hydrofluoric acid solution. The second mixture was then added to the first, and they were brought to the boil under reflux while stirring efficiently.

A separate solution consisting of 332g sodium silicate solution of the type referred to in Examples I and II and 1.6 litre water was then fed slowly into the reaction vessel. The addition was made over a period of about four hours while the reaction mixture was kept boiling and stirred efficiently throughout.

A solution of 76.8g anhydrous sodium carbonate in 1.1 litre water was then made up and this was also added slowly, over a period of about four hours, to the reaction mixture.

The mixture was then boiled under reflux, with efficient stirring for 20 hours. After that, it was filtered under vacuum and washed by filtering 9 litres water through the filter cake. Finally the filter cake was dried in trays at 130°C and ground in a small mill.

The finished product was tested by X-ray analysis and was found to have the same X-ray pattern as hectorite. It had a cation exchange capacity of 90 m.e./100 g.

When 2 g was dispersed in 100 ml cold water, it was found that a clear thixotropic gel was obtained. The gel was heat stable and unaffected by electrolytes even when added in appreciable quantity. By using a rotational (Fann) viscometer, the following rheological parameters were measured on this dispersion:—

Plastic-viscosity	9.0 centipoises
Bingham Yield Value	148.8 dynes/cm²

In this Example the atomic ratios of the constituents in the feed are as follows:—

$$\frac{Si}{F} = 0.89;$$

$$\frac{Li}{Mg} = 0,6;$$

$$\frac{Si}{Mg+Li} = 0.83;$$

$$\frac{Na}{2Mg+F-Li} = 1.0.$$

EXAMPLE IV.

In this Example the procedure of Example III was followed but altering the quantity employed of certain of the constituents. Thus there was employed 5.3 g of lithium carbonate: 23.2 g of sodium hydroxide and 96 ml. of 15% HF solution.

These quantities gave rise to the following atomic ratios of constituents in the feed:—

$$\frac{Si}{F} = 2.22;$$

$$\frac{Li}{Mg} = 0.12;$$

$$\frac{Si}{Mg+Li} = 1.2;$$

$$\frac{Na}{2Mg+F-Li} = 1.0.$$

The product had a cation exchange capacity of 71 m.e./100g. A dispersion of 2 g product in 100 ml. hot water, after cooling, gave a clear thixotropic gel having a plastic viscosity of 9 centipoises and a Bingham Yield Value of 62.4 dyne/cm².

EXAMPLE V.

312g sodium silicate of the type described in the previous examples was diluted with 1.5 litres water. 55g sodium hydroxide and 29.2g lithium fluoride were added and the mixture placed in a 5 litres flask fitted with a stirrer, a heating mantle and a refluxing condenser. A separate solution of 278g magnesium sulphate heptahydrate in 1.5 litres water was them made up and this was added slowly, over a period of about one hour to the reaction mixture, while it was kept boiling and stirred efficiently throughout.

The atomic ratios of the constituents in the feed were thus:—

$$\frac{Si}{F} = 1.35;$$

$$\frac{Li}{Mg} = 1;$$

$$\frac{Si}{Mg+Li} = 0.67;$$

$$\frac{Na}{2Mg+F-Li} = 1.0.$$

The mixture was then boiled, etc. and treated as in the foregoing examples. The product had a cation exchange capacity = 73 m.e./100g and the said values for plastic viscosity and Bingham Yield Value were 6.3 centipoise and 57.6 dynes/cm² respectively.

In general it is found that the higher Bingham Yield Values can be obtained by selecting atomic ratios similar to those of Example III, with a somewhat higher Na ratio, and employing the preferred solids concentration; addition periods, heating times and temperatures.

EXAMPLE VI.

This Example illustrates the emulsion-thickening effect of synthetic products compared with that of a well-known commercial purified natural hectorite product.

The comparison was made on Polyvinyl Acetate emulsions sold by Vinyl Products, Ltd., under the trade names Vinamul N.8800 and Vinamul No.8107. The rheological properties of these emulsions, namely plastic viscosities and Bingham Yield Values, were measured in their original states, after mixing with preformed aqueous clay gels having 25% solid content, and after dilution with the amounts of pure water shown. Addition of either type of clay material as dry powder to the emulsions or diluted emulsions was found to be ineffective, and it was therefore essential to make aqueous gels of them before use for this purpose.

The rheological measurements were done with a rotational (Fann) viscometer.

Composition (weight percentages)				Rheological Properties		
		Clay (dry weight basis)		Added water	Plastic	
N 8800	N 8107	Synthetic	Natural	(inc. water in gel)	Visc. (cp)	Bingham Y.V. (dyne/cm²)
100	0	0	0	0	550	96
95	0	0	0	5	310	130
95	0	1.25	0	3.75	>1000	>48000
95	0	0	1.25	3.75	318	778
0	100	0	0	0	42	101
0	90	0	0	10	14	81.6
0	90	2.5	0	10	67	230
0	90	0	2.5	7.5	16	48

EXAMPLE VII.

This example illustrates the value of a synthetic product in accordance with the invention as an aid in the retention of TiO_2 in paper. The table shows the clear superiority of the synthetic material in this connection. Again, the synthetic material is then incorporated with the paper-making process — being, suitably added to the beater stock.

Type of Titanium Oxide	Retention Aid Used	% Retn. Aid Used Calcd on TiO_2	%TiO_2 Present in Pulp Calcd on dry	% TiO_2 in Sheets	% Retn.	Opacity %	% Brightness
Anatase	—	—	3.92	2.63	67.1	82	95
Anatase	Syn. material	2	3.85	2.96	77.2	82	95
Anatase	natural hectorite product	2	4.48	3.12	69.7	83	95

WHAT WE CLAIM IS:—

1. A synthetic clay-like mineral having the general formula:—

$$\{Si_8[Mg_{6-x}Li_x] \cdot O_{20} \cdot [(OH)_{4-y}F_y]\}^{x(-)} \cdot \frac{x}{n} M^{n(+)}$$

in which x is a value greater than zero and less than 6, y is a value from 1 up to but less than 4, M is a cation and n is an integer from 1 to 3.

2. A synthetic clay-like mineral according to claim 1, in which M = Na^+ and of which 2% by weight dispersion in water has a Bingham Yield Value of 50 to 150 dynes/cm².

3. A synthetic clay-like mineral having the formula:

$$\{Si_8[Mg_{5.47}Li_{0.53}] \cdot O_{20} \cdot [(OH)_2F_2]\}^{0.53(-)} \cdot 0.53Na^+.$$

4. A process for the synthesis of a clay-like mineral as claimed in claim 1 when $M^+ = Na^+$, or as claimed in claim 2, comprising the steps of forming a slurry which contains constituents providing atomic ratios in the ranges

$$\frac{Si}{F} = 0.5 \text{ to } 5.1;$$

$$\frac{Li}{Mg} = 0.1 \text{ to } 1.0;$$

$$\frac{Si}{Mg+Li} = 0.5 \text{ to } 1.5;$$

$$\frac{Na}{2Mg+F-Li} = 1 \text{ to } 2$$

by co-precipitation by slowly combining with heating and agitation in an aqueous medium and in the presence of the lithium and fluoride ions, the constituent providing the magnesium ions with the constituents providing the silicon (as silicate), hydroxyl and sodium ions, hydrothermally treating the slurry for the period as herein defined, washing and dewatering the resultant product and then drying it at a temperature of substantially 110°C to 450°C.

5. A process according to claim 4, wherein the aqueous slurry is formed by heating with agitation an aqueous medium containing the lithium, magnesium and fluoride ions, and slowly adding an aqueous solution of sodium silicate to this medium.

6. A process according to claim 4 or claim 5, wherein the slurry contains constituents providing the atomic ratios

$$\frac{Si}{F} \text{ of } 0.5 \text{ to } 4.0,$$

and

$$\frac{Na}{2Mg+F-Li} \text{ of } 1.0 \text{ to } 1.3.$$

7. A process according to claim 4 for the synthesis of the product claimed in claim 3, wherein the slurry contains constituents providing the atomic ratios

$$\frac{Si}{F} = 2.7;$$

$$\frac{Li}{Mg} = 0.5;$$

$$\frac{Si}{Mg+Li} = 0.9;$$

and

$$\frac{Na}{2Mg+F-Li} = 1.0.$$

8. A process according to claim 6 or claim 7, wherein the dilution of the constituents employed in forming the slurry is such that after the hydrothermal treatment the product is present in amount 1% to 8% preferably about 4% by weight.

9. A process according to any preceding claim 4 to 8, wherein magnesium sulphate and/or chloride is employed to provide magnesium ions.

10. A process according to any of the claims 4 to 9, wherein the step of combining the constituents is conducted over a period of 4 to 6 hrs.

11. A process according to any of the preceding claims 4 to 10, wherein the hydrothermal treatment is conducted over a period of 10 to 20 hrs.

12. A process for the preparation of a synthetic clay-like mineral substantially as described herein with reference to any one of the Examples 1 to 5.

13. A synthetic clay-like mineral whenever produced by a process according to any one of the claims 4 to 12.

14. An aqueous gel of a synthetic clay-like mineral as claimed in any one of claims 1 to 3 or 13.

15. The use of an aqueous gel as claimed in claim 14 in a process for thickening synthetic resin-containing emulsions.

16. The use of synthetic clay-like mineral as claimed in any of claims 1 to 3 or 13, or of an aqueous gel as claimed in claim 14, as a pigment-retention aid in a paper-making process employing titanium dioxide pigment.

For the Applicants:—
GILL, JENNINGS & EVERY,
Chartered Patent Agents,
51/52 Chancery Lane,
London, W.C.2.

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